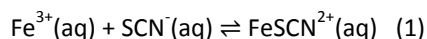


Blood-Red Equilibrium Constant Determination! (DCP)

When chemical substances react, the reaction typically does not go to completion. Rather, the system goes to some intermediate state in which both the reactants and products have concentrations which do not change with time at a particular temperature. Such a system is said to be at chemical equilibrium. This condition is expressed in the equilibrium constant, K_c , for the reaction.

In this experiment, we will study the equilibrium properties of the reaction between the iron(III) ion and the thiocyanate ion:



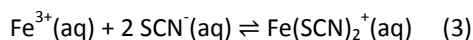
When solutions containing Fe^{3+} ion and thiocyanate ion are mixed, Reaction 1 occurs to some extent, forming the FeSCN^{2+} complex ion, which has a red color. As a result of the reaction, the equilibrium amounts of Fe^{3+} and SCN^{-} will be less than they would have been if no reaction occurred; for every mole of FeSCN^{2+} that is formed, one mole of Fe^{3+} and one mole of SCN^{-} will react. According to our studies, the equilibrium constant expression, K_c , for Reaction 1 is formulated as follows in Equation 2:

$$K_c = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]} \quad (2)$$

The value of K_c in Equation 2 is constant at a given temperature. This means that mixtures containing Fe^{3+} and SCN^{-} will react until Equation 2 is satisfied so that the same value of the K_c will be obtained no matter what initial amounts of Fe^{3+} and SCN^{-} were used. Our purpose in this experiment will be to find K_c for this reaction involving several mixtures made up in different ways as well as to show that K_c indeed has the same value in each of the mixtures. The reaction studied is a particularly good one because K_c is of a convenient magnitude, the color of the FeSCN^{2+} ion makes for an easy analysis of the equilibrium mixture, and the reaction reaches equilibrium quickly.

The mixtures will be prepared by combining solutions containing known concentrations of iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3$, and potassium thiocyanate, KSCN. The color of the FeSCN^{2+} ion formed will allow us to determine its equilibrium concentration. Knowing the initial composition of a mixture and the equilibrium concentration of FeSCN^{2+} , we can calculate the equilibrium concentrations of the rest of the pertinent species and then determine K_c .

In carrying out this analysis, we made the assumption that the reaction which occurred was given by Equation 1. There is no inherent reason why the reaction might not have been:



You might ask how we know whether we are actually observing Reaction 1 or Reaction 3. The line of reasoning is the following. If Reaction 1 is occurring, K_c for that reaction as we calculate it should remain constant with different reagent mixtures. If, however, Reaction 3 is the one that is occurring, K_c should remain constant. By squaring the concentration of SCN^{-} in the equilibrium expression for Reaction 3, the results of the calculation make it clear that Reaction 1 is the one that we are studying.

As a specific example, let us assume that we prepare a mixture by mixing 10.0 mL of 2.00×10^{-3} M $\text{Fe}(\text{NO}_3)_3$ with 10.0 mL of 2.00×10^{-3} M KSCN. As a result of Reaction 1, some red FeSCN^{2+} ion is formed. Its concentration at equilibrium is found to be 1.50×10^{-4} M. Our problem is to find K_c for the reaction from this information. To do this, we first need to find the new initial concentration of each reactant in the mixture due to dilution. Second, we use the equilibrium concentration of the product and the reaction stoichiometry to determine the equilibrium concentrations of the reactants. Since the product was formed at the expense of reactants, we can calculate the amount of each reactant that was used up. In the third step, we use these equilibrium concentrations to evaluate K_c for the reaction.

To determine the $[\text{FeSCN}^{2+}]$ in the equilibrium mixtures, we will use a spectrophotometer, which measures the amount of light absorbed by the red complex at 447 nm, the wavelength at which the complex most strongly absorbs. The absorbance, A , of the complex is proportional to its concentration, M , and can be measured directly on the spectrophotometer, colorimeter, or SpectroVis. Review of Beer's Law and a review of how the SpectroVis is operated might be useful. Once the absorbance value is recorded, use the value $k = 5.00 \times 10^3$ to determine the concentration (M) of FeSCN^{2+} for each solution using the equation $A = k c$ where A is absorbance, k is a constant, and c is the concentration. See below on Beer's Law for why this "simplified" equation is used.

The Beer-Lambert Law

Now let us look at the Beer-Lambert law and explore its significance.

$$A = \epsilon bc$$

- Where **A** is absorbance (no units, since $A = \log_{10} P_0 / P$)
- **ϵ** is the molar absorptivity with units of $\text{L mol}^{-1} \text{cm}^{-1}$
- **b** is the path length of the sample - that is, the path length of the cuvette in which the sample is contained. We will express this measurement in centimeters.
- **c** is the concentration of the compound in solution, expressed in mol L^{-1}

The reason why we prefer to express the law with this equation is because absorbance is directly proportional to the other parameters, as long as the law is obeyed. We are not going to deal with deviations from the law and therefore we can assume that **ϵb** is a constant (**k**) for this material and is provided above.

Procedure:

Label eight regular CLEAN, DRY (>25mL) test tubes BkA, BkB, BkW, and 1 to 5 and place them in a test tube rack. Use the set up buret to deliver the appropriate amount of each reactant into the test tubes. The following is provided to give you a guide to aim for, but YOUR data will most likely be different. The reagents to be added for each mixture are summarized:

Tube #	BkA	BkB	BkW	1	2	3	4	5
Volume $\text{Fe}(\text{NO}_3)_3$ solution (cm^3)	10.00	0.00	0.00	10.00	10.00	10.00	10.00	10.00
Volume KSCN solution (cm^3)	0.00	10.00	0.00	2.00	4.00	6.00	8.00	10.00
Volume DI H_2O (cm^3)	10.00	10.00	20.00	8.00	6.00	4.00	2.00	0.00

*The BkA, BkB, and BkW are blanks for $\text{Fe}(\text{NO}_3)_3$, KSCN, and DI water respectively.

Mix each solution thoroughly with a glass stirring rod. Be sure to DRY THE STIRRING ROD AFTER MIXING EACH SOLUTION or else you will dilute and contaminate your solutions.

Calibrate the instrument at 447 nm. Place a (5cm^3 or $2/3$ full) portion of the mixture from tube 1 in a cuvette and measure the absorbance of the solution at 447 nm. Complete each measurement 3-4 times depending on sample available. You may average these values to use for calculations. Repeat the measurement using the mixtures in each of the other test tubes. You must determine the initial concentrations of each ion prior to equilibrium taking into account dilution. Determine the final concentration of FeSCN^{2+} using the simplified Beer's Law. The final equilibrium concentrations for each of the reactants must also be determined. Calculate K_c assuming the reaction:

